Chemical and Mechanical Mechanisms of Moisture Damage in Hot Mix Asphalt Pavements

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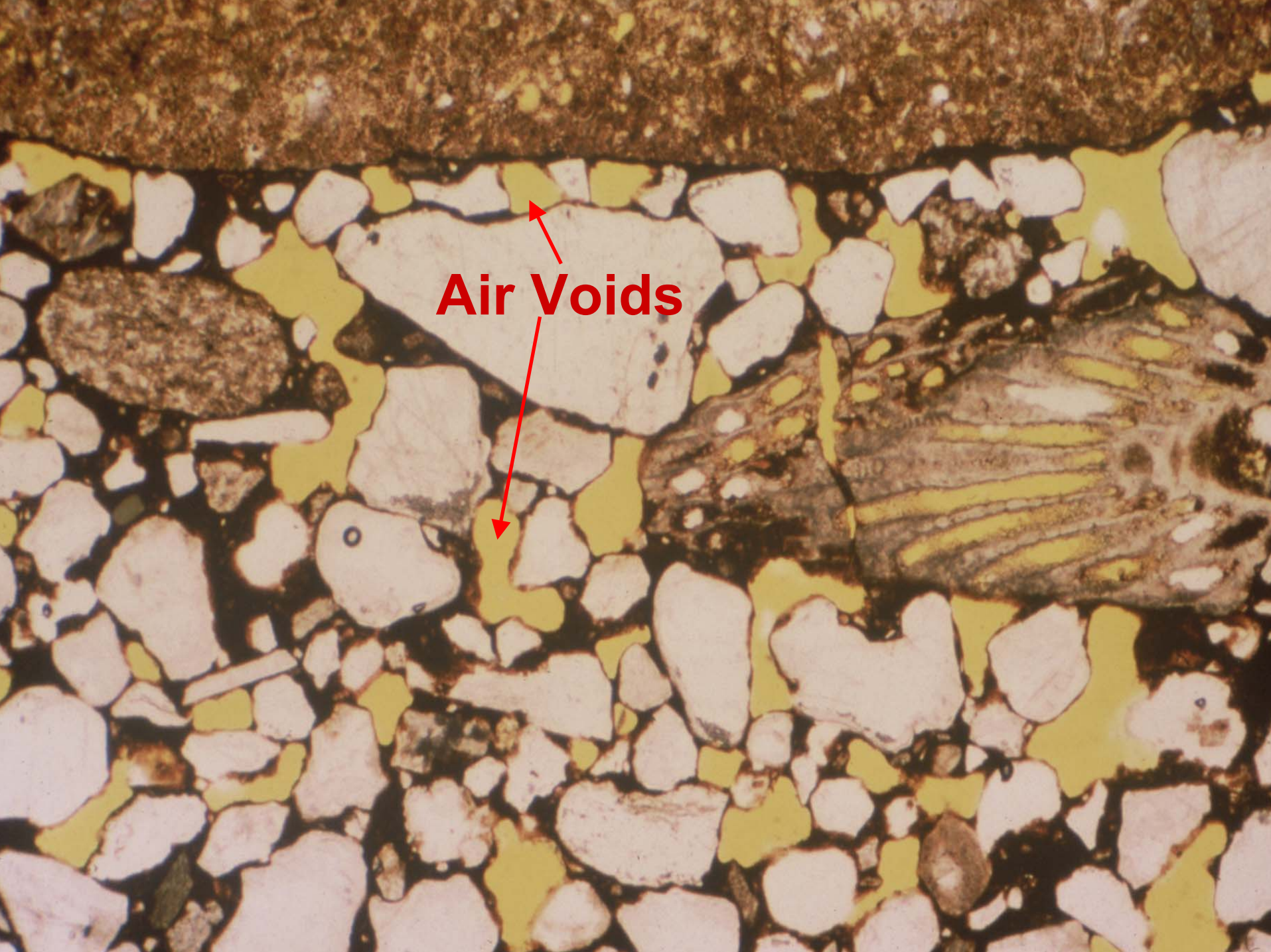
Moisture Damage – Loss of strength and durability due to effects of Moisture

loss of bond

weakening of mastic


Air Voids

The literature suggests a number of mechanisms

- Detachment
- Displacement
- Spontaneous emulsification
- Pore pressure
- Hydraulic scour
- pH instability
- Environmental effects

Adhesion Theories

- Chemical reaction
  - Overall polarity of organic molecules promotes attraction to polar aggregate
  - Charges are non-uniform (no net charge)
  - Aggregate charge distribution affected by environment
  - Some polar components of asphalt adhere more tenaciously and with more durability than others

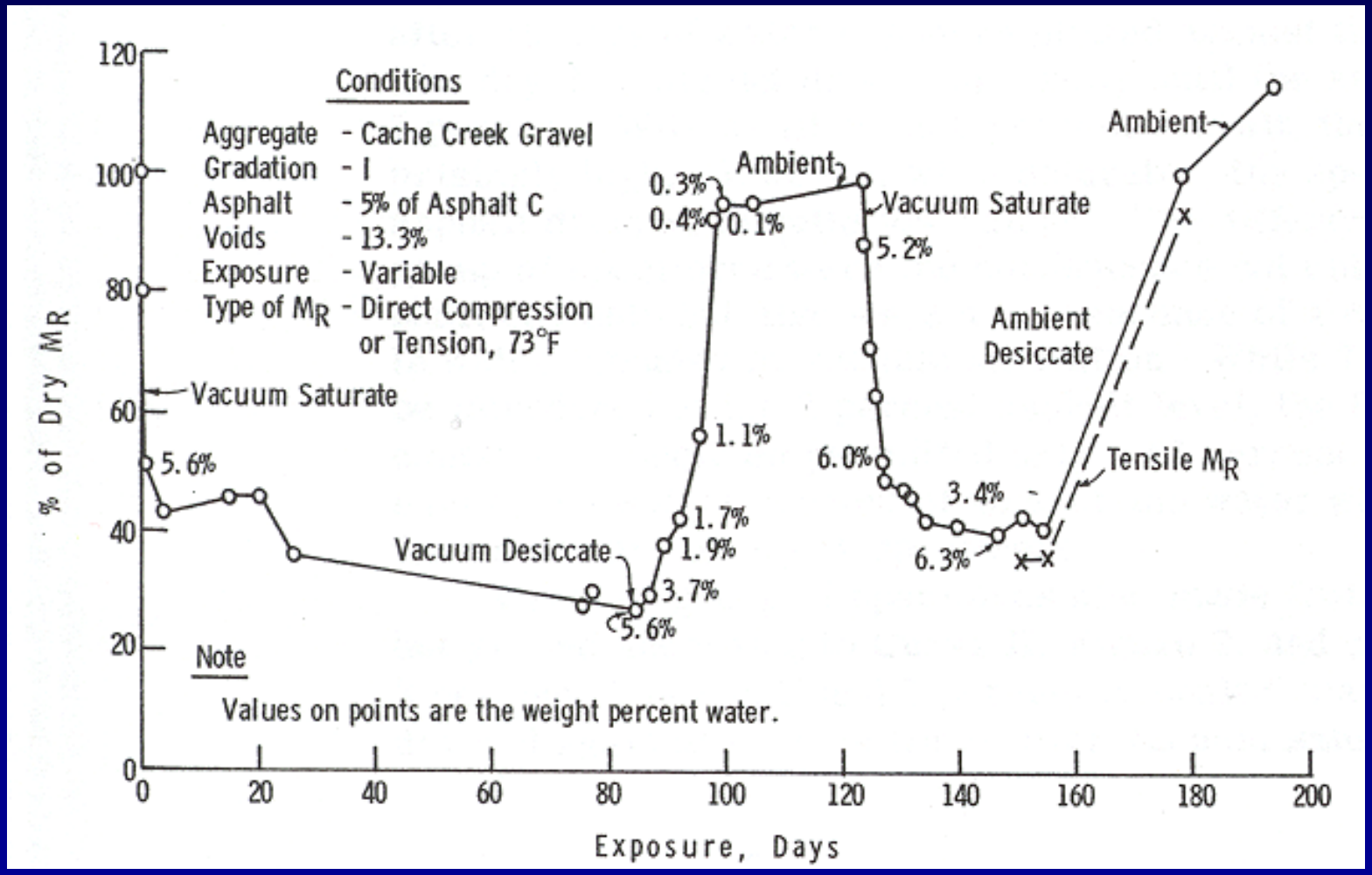
Adhesion Theories, cont'd

- Surface energy and molecular orientation
  - Associated with wetability
  - Synergistic effects
  - Surface energy defines bond strength
- Mechanical
  - Function of: surface texture, porosity, surface coatings, surface area, particle size
  - Seek to maximize area and provide acceptable texture

Cohesion

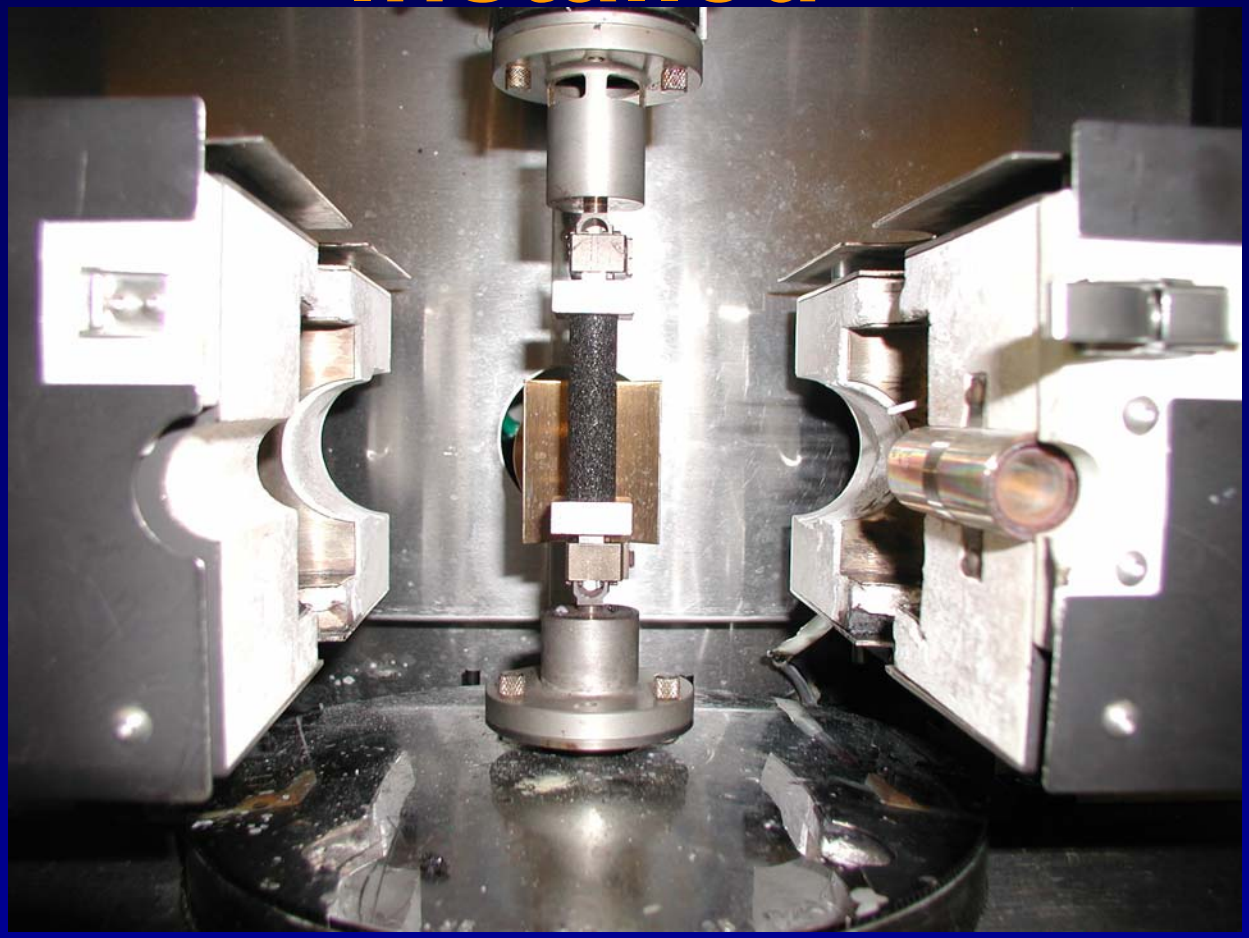
- Influenced by mastic rheology
  - Function of asphalt binder and filler
  - Terrel and Al-Swailmi – describe how water can weaken by saturation and void swelling
  - Illustrated by classic Schmidt and Graf (1972) experiment

Reversible Effect of Moisture on M_r

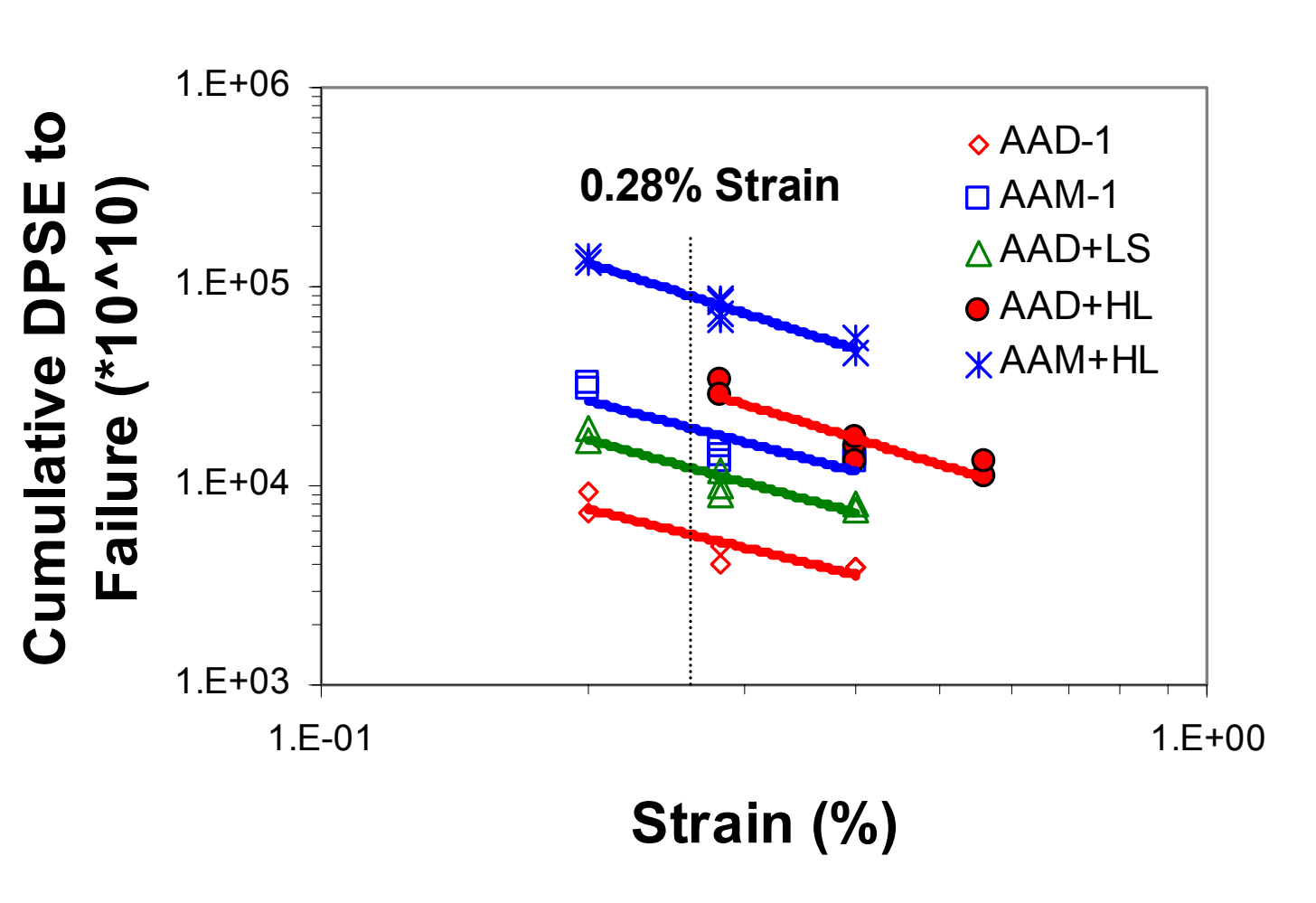


Schmidt and Graf, 1972

Sand-asphalt Sample Installed



Impact of Mineral Filler on Resistance Of Mastic to Damage

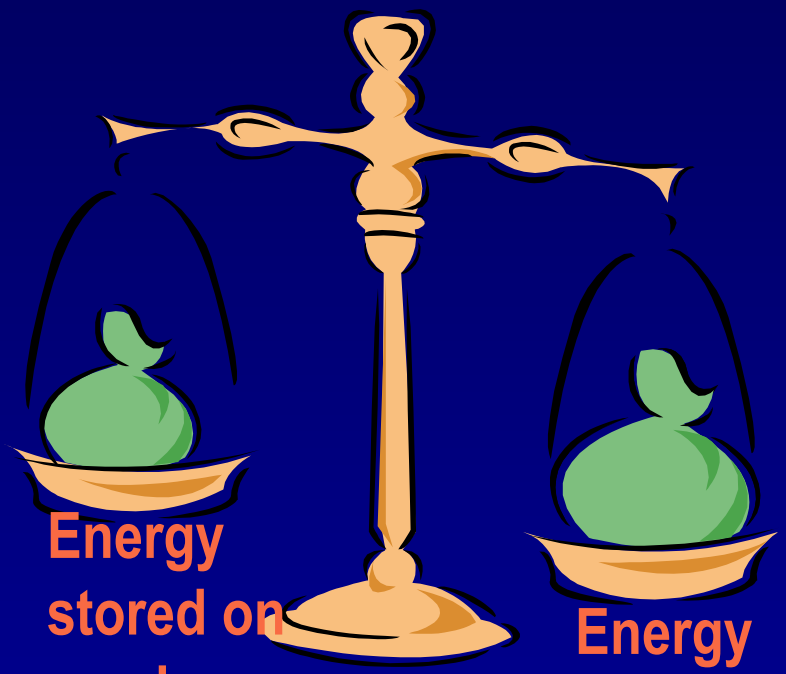


Surface Energy Measurements: Wilhelmy Plate and USD

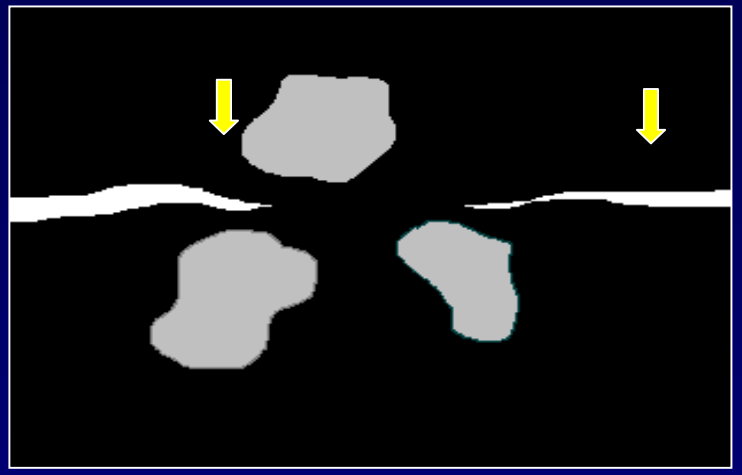
Bitumen-aggregate Bond is calculated From surface free energy

Start with Schapery's First Principles Fracture Theory

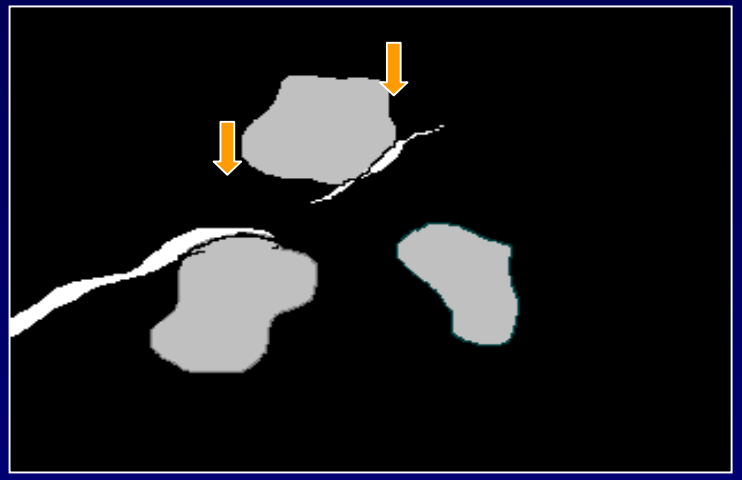
- Load-induced energy that causes fracture
- Balanced by energy stored on newly formed cracks



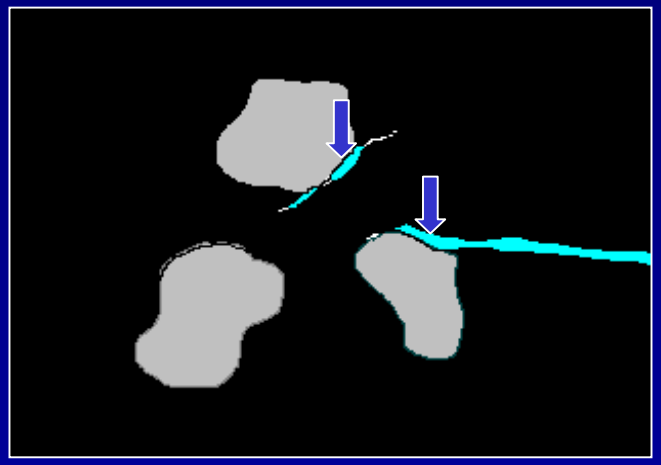
Cohesive Fracture



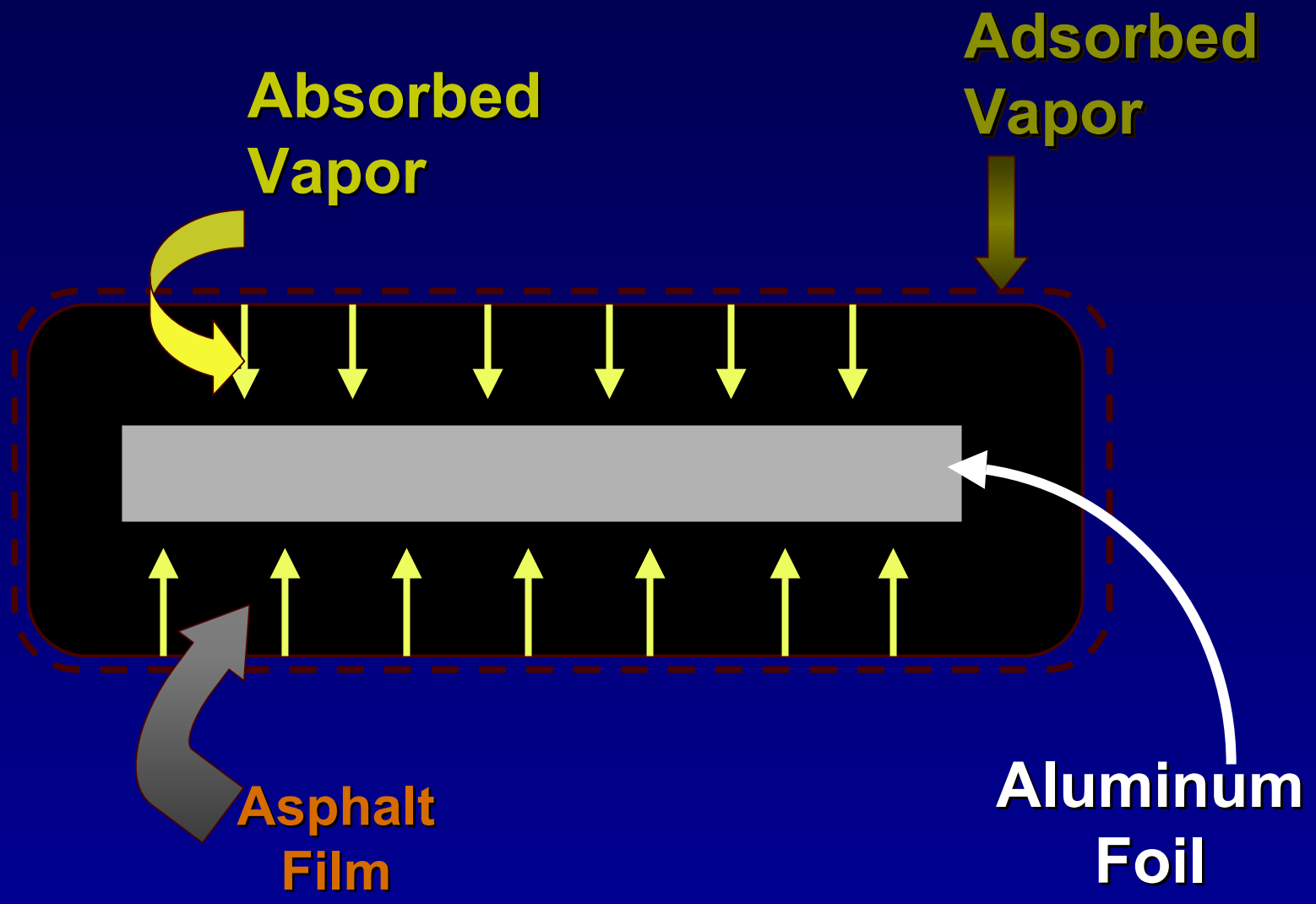
Adhesive/Dry



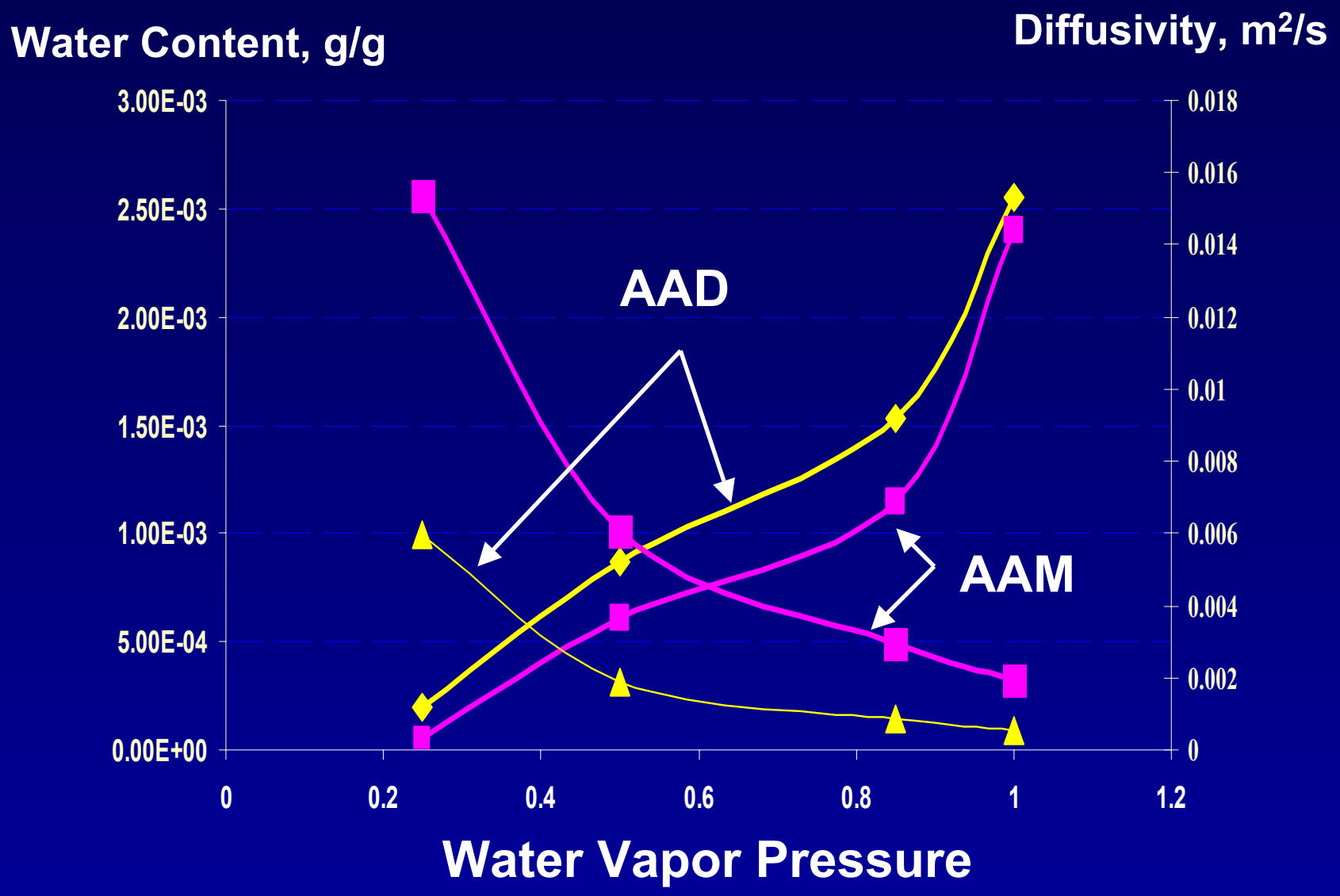
Adhesive/wet



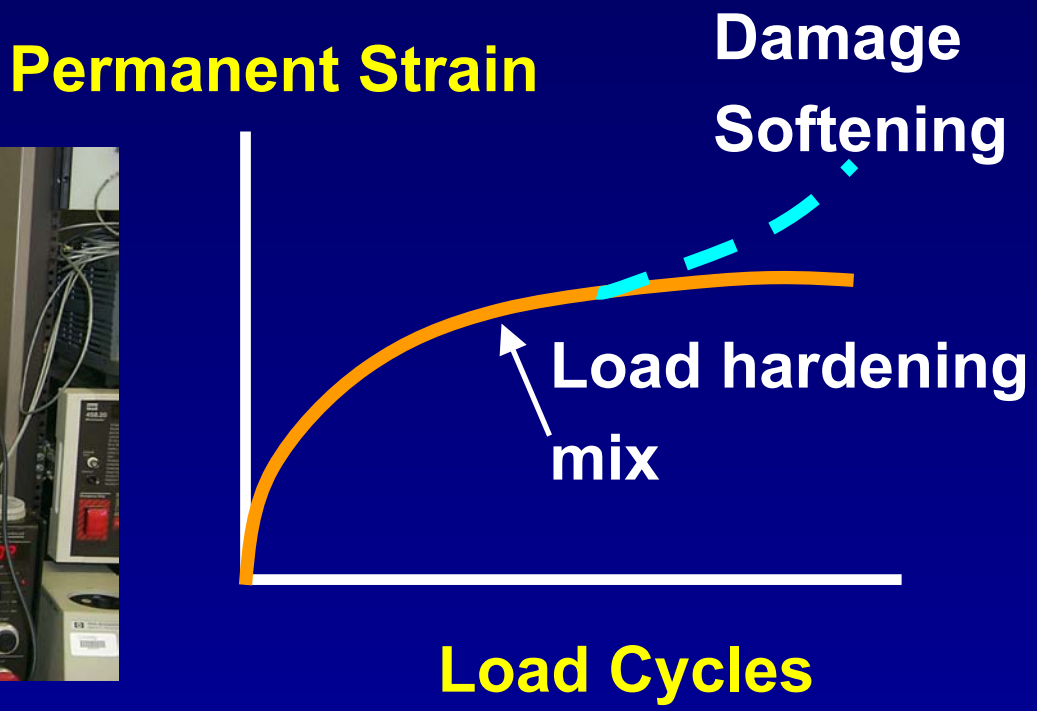
Measure of adsorbed and absorbed Solutes



Diffusivity and Absorbed Water



Laboratory Damage Evaluation



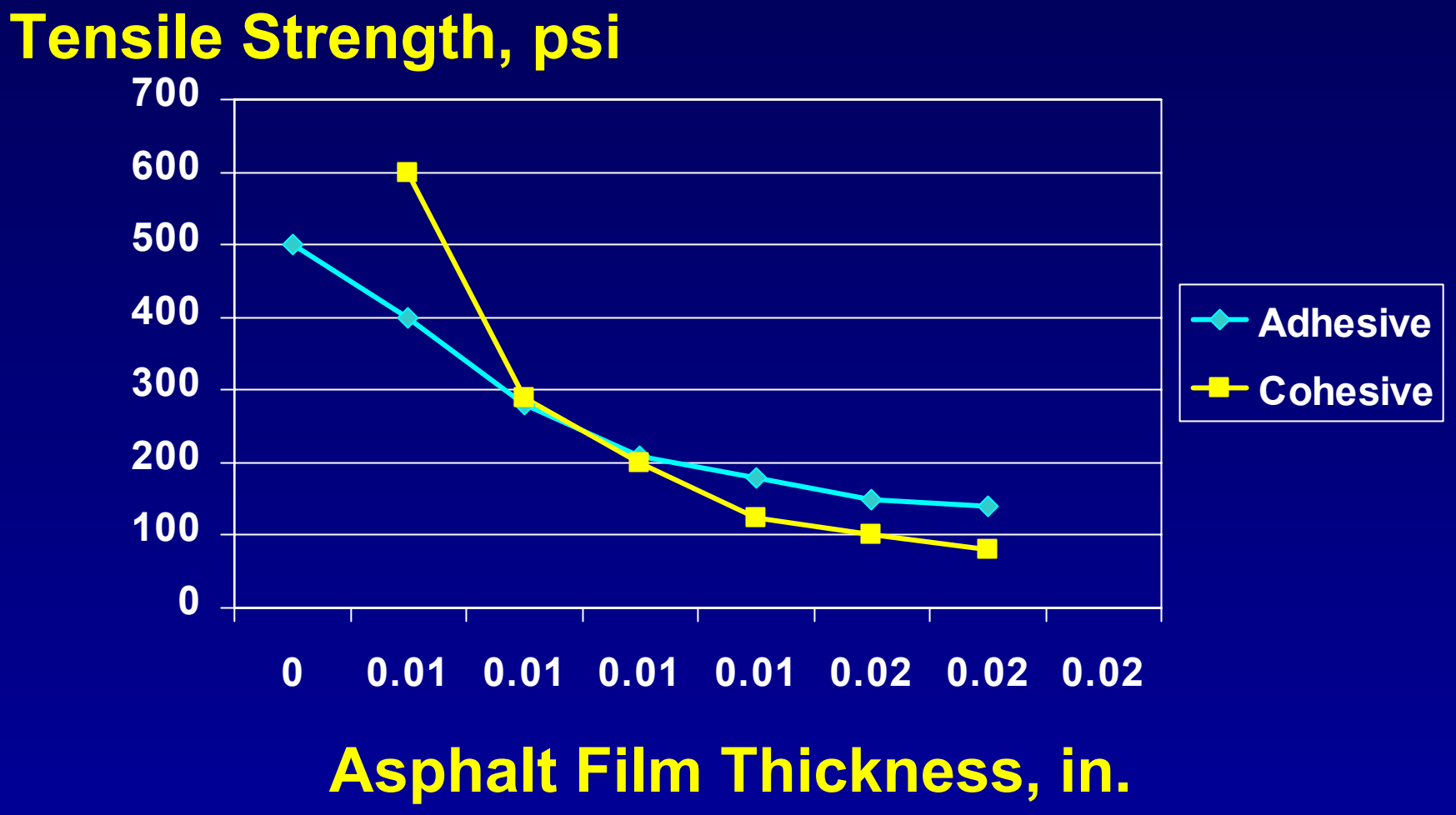
458.20
GARDNER SYSTEMS
READOUT SELECTOR
SET POINT
START
STOP

Comparison of Free Energy of Adhesion (ergs/cm^2) and Triaxial Testing (Saturated)

Mix	Cycles to accel. damage	Free energy of adhesion (dry)	Free energy of adhesion (wet)
DLS	425	141 (614)	-67
MLS	550	205 (889)	-31
DGG	350	153 (158)	-48
MGG	455	199 (206)	-30

values in ( ) represent ergs/gm x 10^3

Adhesive v. cohesive bond failure: a function of film thickness



Effect of Asphalt Composition

- No net asphalt charge but non-uniform charge distribution
- Aggregate surface charges also vary widely
- Charge arises from polar-polar attraction
- Strength and tenacity of bitumen-aggregate bond a function of asphalt polar component

Tenacity and Durability Asphalt Component to Bond with Aggregate

- Robertson (2000)
  - Nitrogen compounds held tenaciously
  - Monovalent salts of acids (RCOOH) are water susceptible
  - Divalent salts of acids are moisture resistant
- Curtis (1992)
  - Sulphoxide > carboxylic acid > non-basic nitrogen / ketone > basic nitrogen > phenol
  - But sulphoxide and carboxlyic acid susceptible to moisture

Effect of Aggregate Properties

- Pore volume and area
  - Yoon and Tarrer (1988) – bond defined by surface area, pore volume, pore size
  - Asphalt penetration synergistically dependent on pore size and asphalt viscosity

Effect of Aggregate Properties, cont'd

- pH of contacting water
  - Hughes et al. (1960) and Scott (1982) – bond in presence of water weakens as pH increased from 7 to 9

Effect of Aggregate Properties, cont'd

- pH of contacting water, cont'd
  - Tarrer (1988) – pH of aggregate fines in water will become asymptotic to relatively high levels
    - Approx. 10 for limestone
    - Approx. 8.8 for granite
    - Approx. 8 for quartz sand and gravel
    - Approx. 7 for chert gravel

- pH of contacting water, cont'd
  - Yoon and Tarrer (1988) – aggregate selectively adsorbs some asphalt components and H-bonds or salt links are formed
  - Yoon and Tarrer (1988) – Presence of ketones and phenols are important to reduce stripping resistance; carboxylic acids, anhydrides, and 2-quinolones increase moisture sensitivity

- pH of contacting water, cont'd
  - Thomas (2002) – interaction of moisture sensitive components from asphalt with hydrated lime may also allow bonds with nitrogen compounds to proliferate
  - Thomas (2002) also points out that lime may react with asphalt components that can further oxide to increase viscosity

- pH of contacting water, cont'd
  - Yoon and Tarrer (1988) – metal ions affect stripping
  - Alkaline earths for salts not easily dissociated in high pH
  - Hydrated lime can tie up carboxylic acids and 2-quinolones and prevent them from interacting with H-bond forming functionalities

Interaction of alkaline aggregates and asphalt with acidic components

$$CaC0_3 + 2RC00H \rightarrow (RC00^-)_2\ Ca + CO_2 + H_20$$

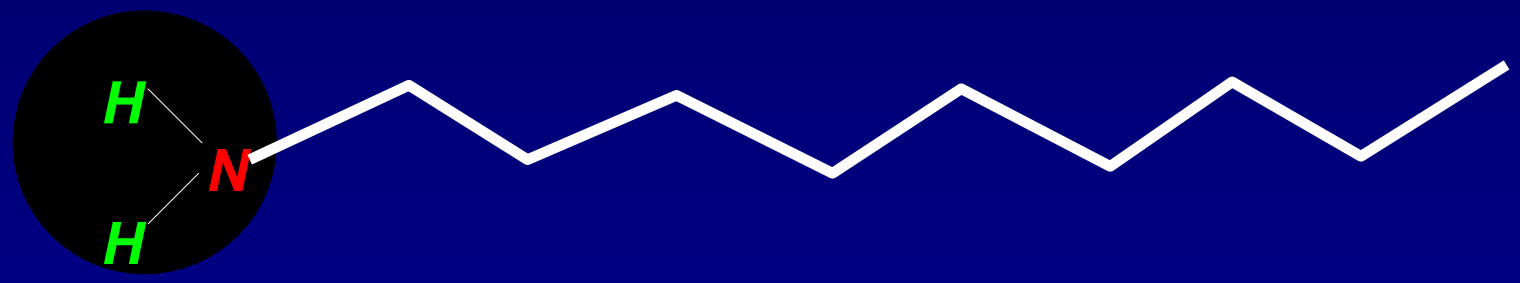
$$CaO + 2RC00H \rightarrow (RC00^-)_2\ Ca + H_20$$

$$Ca(OH)_2 + 2RC00H \rightarrow (RC00^-)_2\ Ca + 2H_20$$

In a similar manner to reaction between acidic compounds and alkaline aggregates or hydrated lime, amine compounds present in asphalt or added in the form of antistripping agents can will react with acidic surfaces as in the case of siliceous aggregates to form a surface compound.

Interaction of acidic aggregates and asphalt with alkaline amine components

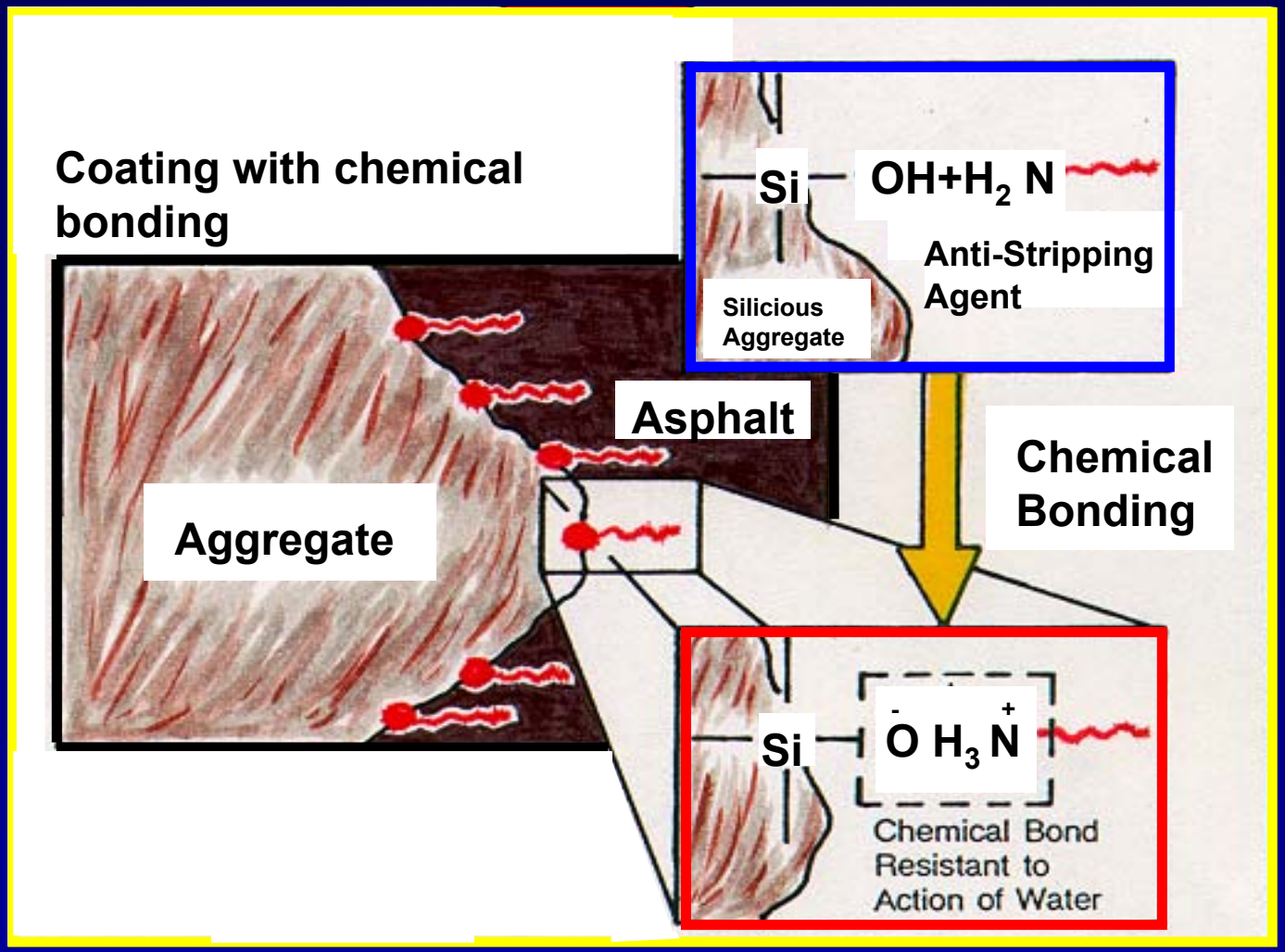
$$--SiOH + RNH_2 \rightarrow --SiO^- RN^+H_3$$



Polar End Group

Non-Polar Hydrocarbon Chain

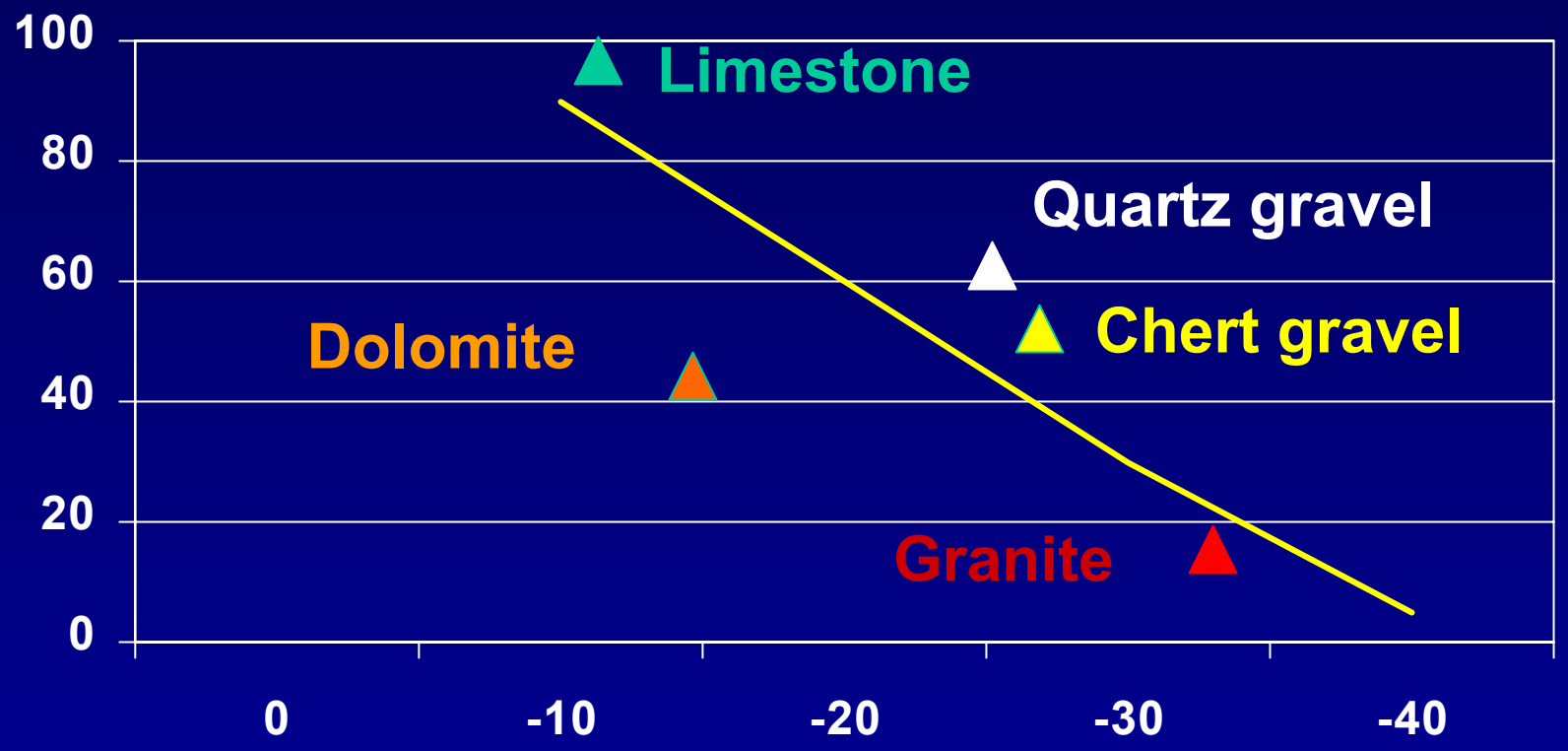
Asphalt aggregate interaction in the presence of suitable compounds in asphalt



Surface Potential

- R-COOH in asphalt forms $R\text{-}COO^-$ and H^+ causing asphalt surface to have negative polarity at the interface
- Aggregate in presence of water is also negative – repulsion
- As pH of the water increases – negative charge becomes greater

Yoon and Tarrer (1988) Used Zeta Potential to Measure Aggregate Surface Charge

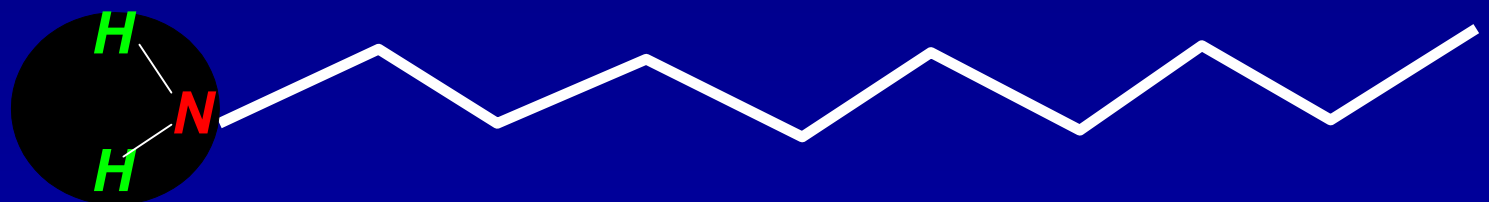


SHRP Adhesion Model

- Stripping controlled by cohesive failure within aggregate rather than at bitumen-aggregate interface
- Surface rich in alkaline earth metals promote formation of water-insoluble salts and are more moisture resistant
- Stripping of siliceous aggregates may occur due to dissociation of silica generated by solubilization of alkaline earth cations and soaps formed between acid anions (bitumen) and alkali metal cations on aggregate surface

Methods of Improvement

- Interaction of acidic aggregates with alkaline amine compounds
  - Amine ionized to R-NH_3 with positive charge
  - Length of hydrocarbon chain (R) and number of amine groups influence adhesion
  - Fatty amines enable asphalt to wet aggregate surface
  - Hydrophobic, hydrocarbon chain of the fatty amine is anchored in bitumen (bridge)

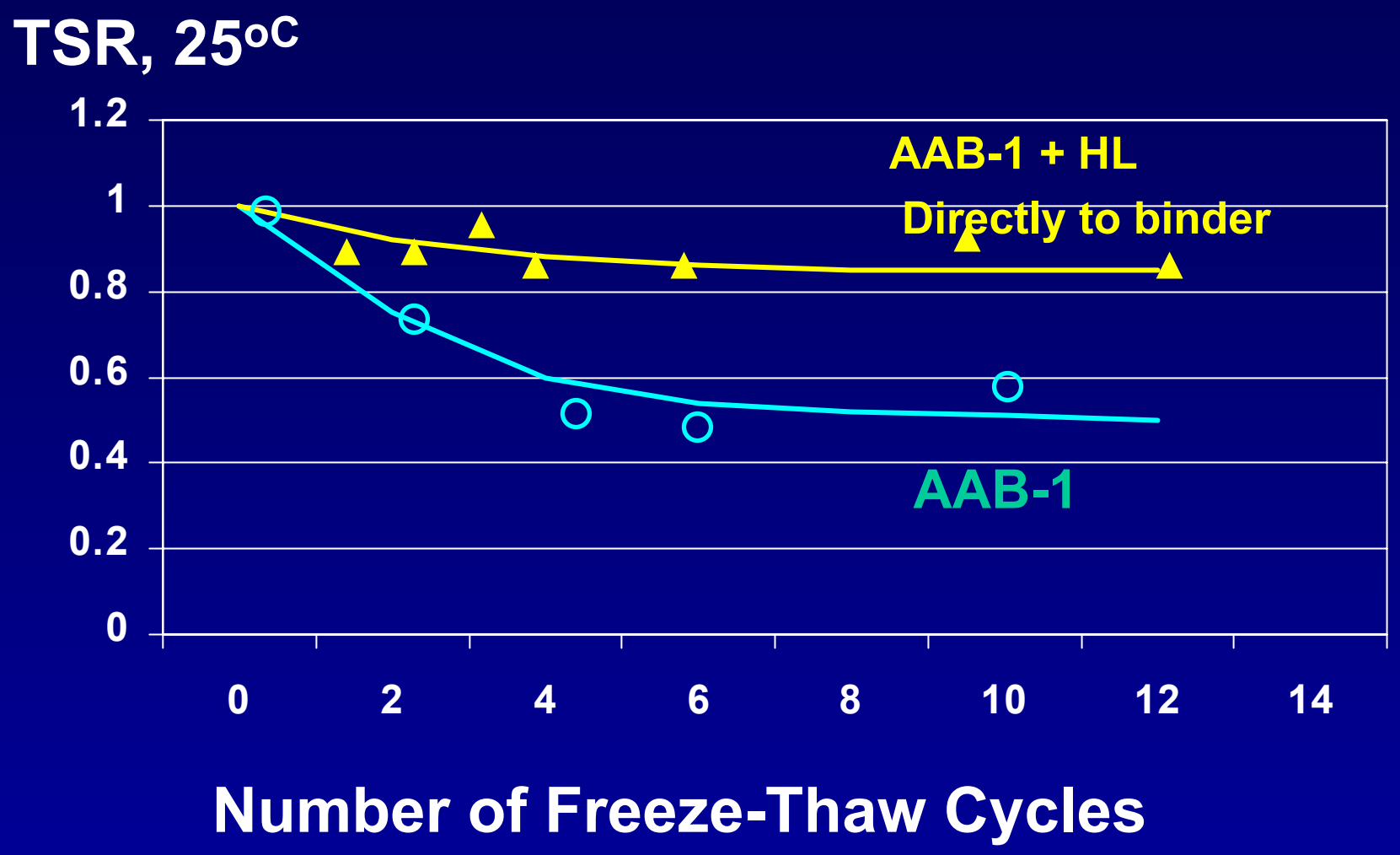


Methods of Improvement, cont'd

- Hydrated lime
  - In siliceous aggregates, H-bond between H_2O and and aggregate SiOH group is preferred over that between SiOH and COOH
  - $Ca(OH)_2$ provided Ca^{++} to react with COOH to allow stronger bond with nitrogen groups (Petersen et al., 1987)
  - Ca^{++} also migrates to aggregate surface to replace H^+, Na^+, K^+, and other cations (Schmidt and Graf, 1972)

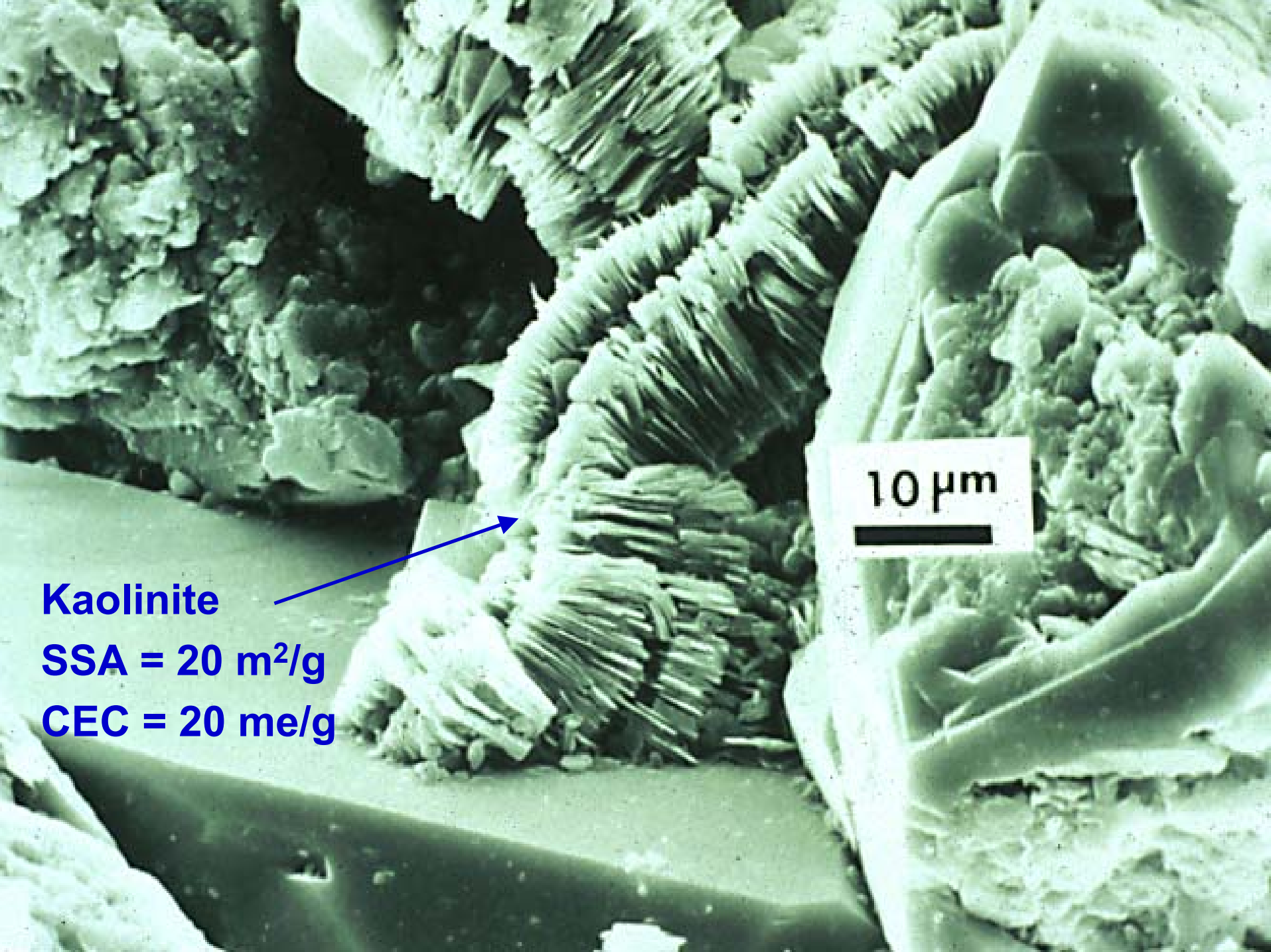
- Hydrated lime, cont'd
  - Mg and Ca salts are relatively hydrophobic, not very soluble
  - RCOOH in bitumen bonds very strongly with aggregate surface, but high sensitive to moisture disruption
  - Conversion of RCOOH to Ca^{++} based salts before mixing with aggregate could prevent adsorption of water-sensitive free acids to begin with
  - Could hydrated lime introduced in the refinery or at the plant achieve this? (WRI, 1997)

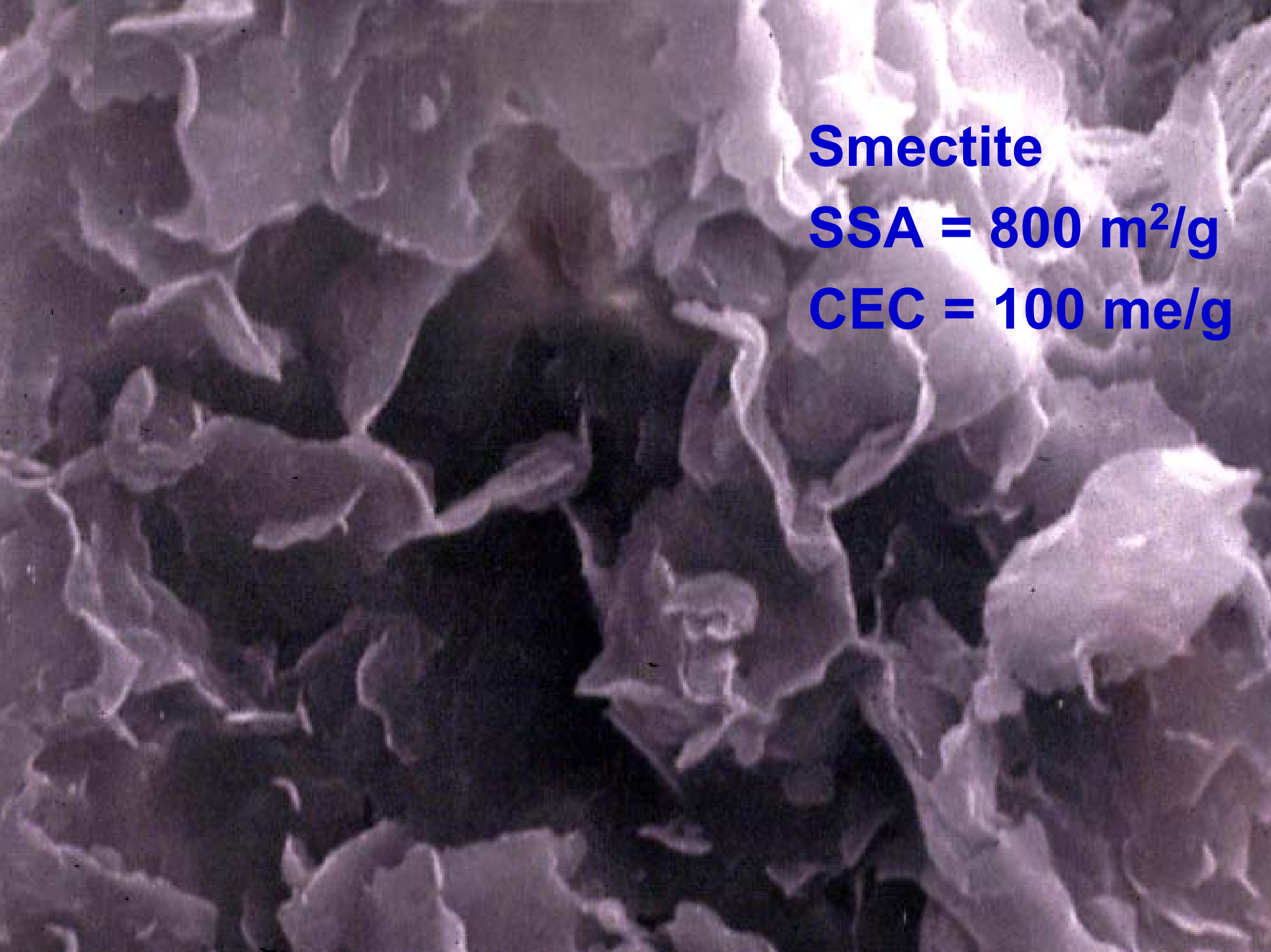
Impact of Freeze/Thaw Cycles on TSR



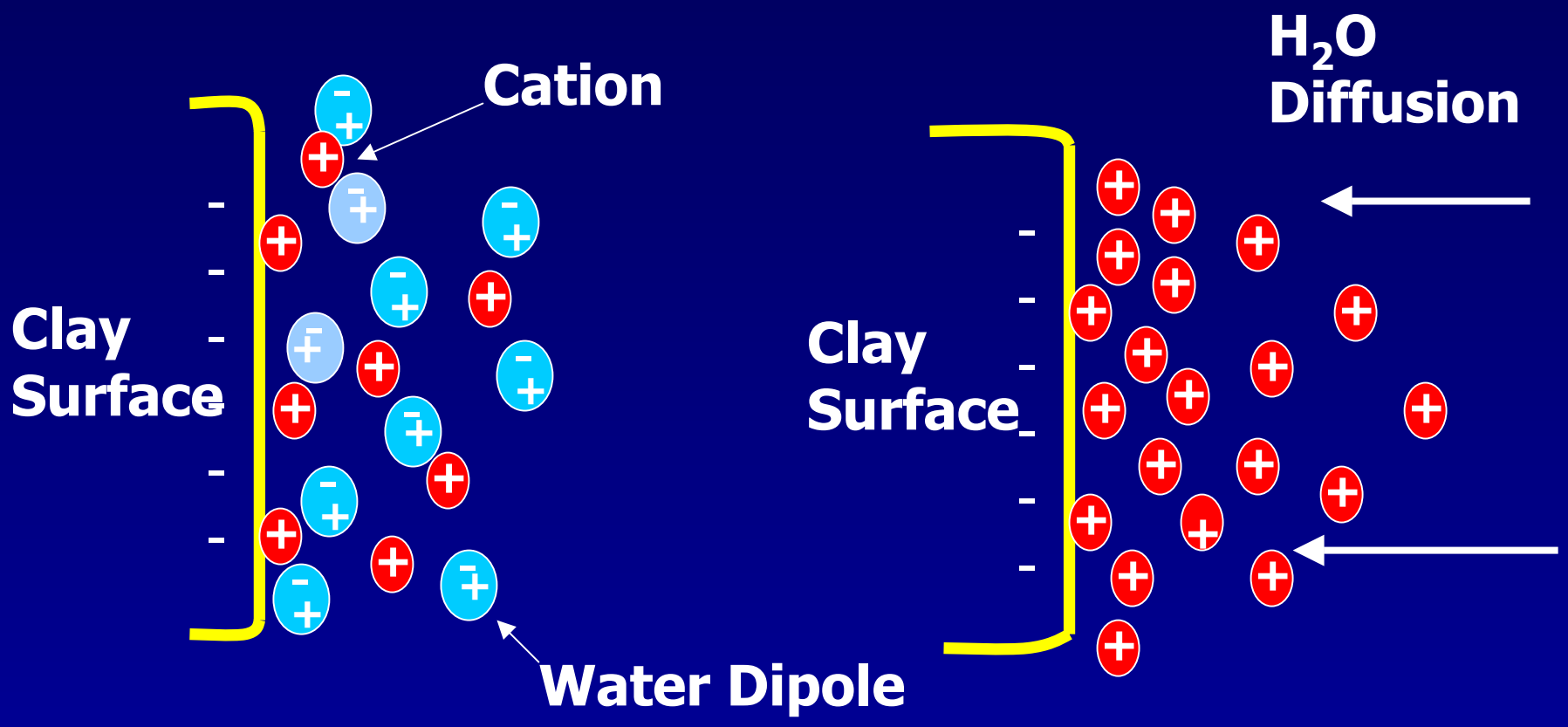
Dusty and Dirty Aggregates

- Dusty – coated with materials smaller than 75 μm – interruption of bitumen-aggregate bond
- Dirty – coated with clay minerals
  - high surface area
  - negative charge
  - affinity for water


10 μm
Kaolinite
SSA = 20 m²/g
CEC = 20 me/g

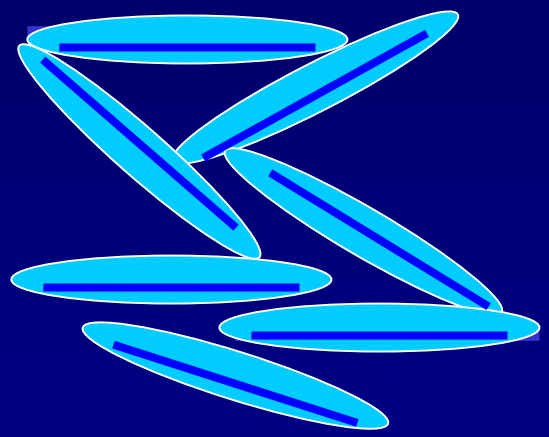

Smectite
SSA = 800 m²/g
CEC = 100 me/g

Double Diffused Water Layer (DDL)

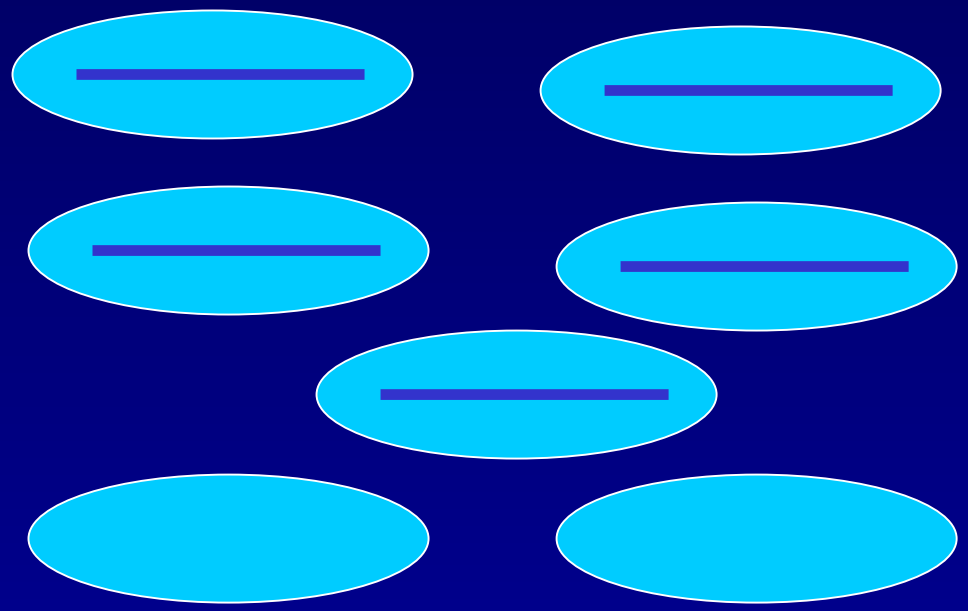


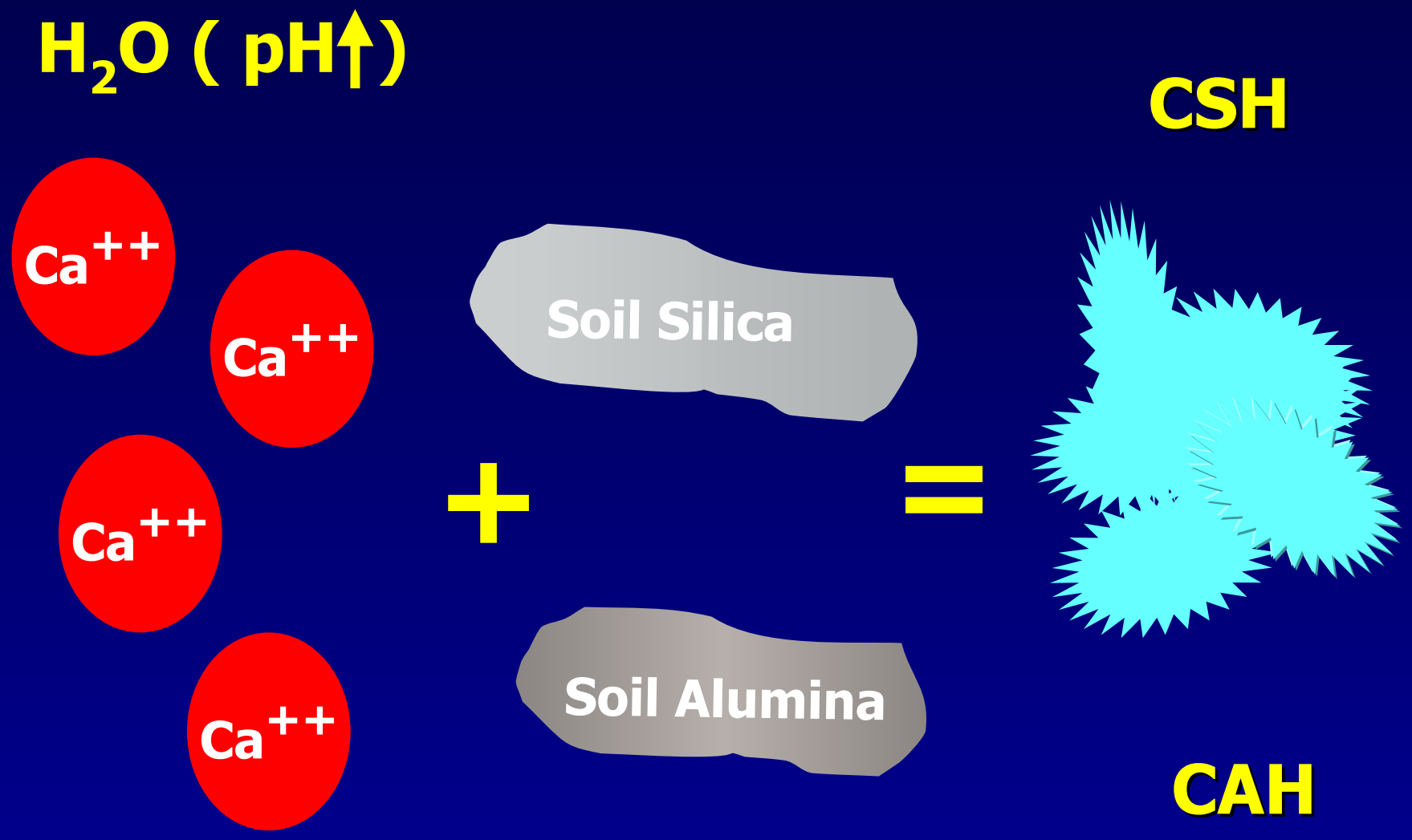
Effect of Cation Adsorption on Attracted Water Layer

Ca^{++} Saturation



Na^{+} Saturation




H_2O (pH↑)
Ca^{++}
Ca^{++}
Ca^{++}
Ca^{++}
Soil Silica
+
Soil Alumina
=
CSH
CAH

Conclusions

- Moisture damage a synergistic process
- Non-uniform distributions in asphalt and aggregate produce bond
- Certain asphalt polars produce a more tenacious and durable bond
- Bond is affected by aggregate mineralogy, texture, and porosity

Conclusions, cont'd

- In addition to strong bond, asphalt must be able to wet and penetrate surface voids
- Bond is dynamic and is affected by pH shifts
- Moisture resistance is derived not only from bond strength but also mastic strength